Sulfated Ce_xZr_{1-x}O₂ oxides. Surface properties and performance for methane oxidation under fuel-rich conditions

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Abstract

Two series of sulfated zirconia-ceria based catalysts have been prepared by coprecipitation of the Zr⁴⁺ and Ce³⁺ salts. The Zr-Ce-O samples, with Zr/Ce ratios ranging from 1 to 15, were then sulfated by impregnation using H₂SO₄ and [(NH₄)₂S₂O₈]. The textural, structural and surface characteristics of the resulting modified catalysts were revealed by N₂ adsorption-desorption, XRD, XPS spectroscopy and TPD of NH₃, and results were connected with their catalytic behaviour. Then the catalysts were tested in the direct conversion of methane at high temperature (650 °C) under fuel-rich conditions. Experiments were conducted using low O₂/CH₄ ratio mixtures and high space velocity. It was shown that O₂/CH₄ feeds resulted in practically

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total combustion of CH₄ when sulfated/persulfated ceria–zirconia catalysts are used, while surface acidity plays a crucial role on the extent of deep oxidation reactions.

Keywords: ceria–zirconia mixed oxides, acidity, surface characterization, partial oxidation of methane.

1. Introduction

Methane valorization by partial oxidation to methanol or formaldehyde, though tempting, remains still rather an elusive perspective. Indeed, methane is characterized by its chemical inertness because the sp³ hybridization of C-atom which results in a high C–H bond stability (440 kJ/mol). Unfortunately, once activated, it is rare to obtain the partial oxidation products as they are more reactive than the substrate itself and the reaction proceeds rapidly leading to a CO₂ release [1]. Generally, redox properties are claimed to be responsible for the catalysts performance in oxidation reactions [2] although the acid–base strength was also suggested to play a vital role in the initial step of C–H activation [3].

Redox-type catalysts perform the direct CH₄ conversion at temperatures in the region 400–650 °C under fuel-rich mixtures and high space velocity to minimize the extent of the more thermodynamically favorable combustion reaction which produces unwanted CO_x [1,4,5]. Several recent reviews covering various aspects of the direct partial oxidation of methane to oxygenates have been reported [1,6,7]. However, the CH₄ conversion on solid acid catalysts has been much less studied. Strong solid superacids such as sulfated zirconia (SZ) [8–11] and heteropolyacids [12–144] have been claimed to

1 be active in the conversion of light alkanes under relatively mild reaction conditions.
2 Pioneering works by Moffat *et al.* [12] on the oxidation of methane over supported
3 heteropolyacids (HPA) at temperature between 520–570 °C and atmospheric pressure
4 using nitrous oxide or oxygen as oxidant demonstrated small conversions of methane
5 with CO and CO₂ as the main reaction products with significantly smaller amounts of
6 HCHO and traces of methanol. These seminal studies highlighted the capacity of HPA
7 to promote selective oxidation.
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17 More recently, He *et al.* [13] synthesized mesoporous silica containing an HPA, whose
18 structure was destroyed upon calcination at 600 °C. The resulting mixed oxide was
19 active in the gas-phase selective oxidation of methane with only O₂ at atmospheric
20 pressure. The catalyst led only to the formation of HCHO (together with CO and CO₂)
21 with the highest space-time yield of HCHO (330 g_(HCHO)/h kg_{cat}). Besides this, the
22 nature of the catalytic site remains poorly understood as the HPA has been restructured
23 during the catalyst preparation. In addition, preparation of HPA using a classical
24 impregnation method yields a significantly lower yield for a similar loading and
25 temperature (about 1%). So the most active species must differ from the classical
26 Keggin unit. It should be noted that conversion increases with the temperature,
27 regardless of the loading, while the selectivity decreases. Hence, the temperature is
28 optimal around 640 °C when considering only the yield.
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47 In addition to heteropolyacids, zirconia–ceria (Zr–Ce–O) catalysts have been widely used
48 in catalysis for their excellent thermal stability, ability to release/store oxygen and
49 exceptional acidity properties (as Zr⁴⁺ and Ce⁴⁺ act as Lewis acid sites) [15–17]. A
50 major problem was, however, that it deactivates rapidly in absence of oxygen and it
51 exhibits small lifetime which prevent its direct use in commercial processes. In order to
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improve the performance of sulfated zirconia, many alternatives were used as the addition of noble metals [18] or transition metals such as iron or manganese [199].

The approach of sulfated $\text{ZrO}_2\text{-CeO}_2$ oxides as possible catalysts for the direct oxidation of methane to C1 oxygenates is an attempt to combine and study the participation of both redox and methane activation sites. Their capability for oxygen releasing would produce oxygen vacancies and also cationic sites with defective low oxidation states which allow the transfer of charge between sites. The addition of acidic oxides (such as sulfates) has been used in order to improve the low-temperature hydrocarbon oxidation activity, since they have oxidizing properties, producing intermediates (cations) formed by one electron abstraction [2020,221].

The aim in the present work was to examine the surface and structural characteristics of sulfated and persulfated Zr-Ce-O solid mixed solutions to connect them with the catalytic behaviour in the partial oxidation of methane under fuel rich conditions, studying also the influence of a low proportion of nitric oxide in the reactant feed on the catalytic behaviour of both acidic zirconia-ceria series.

2. Experimental

2.1 Preparation of ZrCeO substrates and S-loaded ZrCeO

Sulfated and persulfated ZrCeO ($x\text{-SO}_4$ and $x\text{-S}_2\text{O}_8$, respectively) catalyst series were prepared by adopting a two-step methodology. In the first step a Ce-Zr hydroxide gel substrate was prepared while in the second one sulfate or persulfate ions were incorporated by a conventional impregnation methodology. The $\text{Ce(OH)}_3\text{-Zr(OH)}_4$ hydroxides ($x = \text{Zr/Ce}$ mole ratio) were obtained by precipitating the Ce^{3+} and Zr^{4+} ions

from an aqueous solution of the corresponding salts (cerium nitrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, Aldrich] and zirconium oxychloride $[\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}]$, Aldrich]) with a dilute (0.1 mol/L) aqueous ammonia solution. Precipitation was performed under vigorous stirring until a final pH of 8.0 was reached. Then the precipitate was aged for 2 h and finally filtered off, washed repeatedly and dried at 110 °C for 12 h. Following this procedure, four samples with Zr/Ce molar ratios of 1, 5, 10 and 15 were obtained. Each sample was split in two identical portions: in one of them sulfate was incorporated while the other was modified with persulfate. For this purpose, the dried hydroxide gel $[\text{Ce}(\text{OH})_3\text{-Zr}(\text{OH})_4]$ was treated with either aqueous H_2SO_4 solution (one portion) or aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution (second portion). The volume of 0.5 mol/L H_2SO_4 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution was selected in order to reach an equivalent amount of 15 mL of pure H_2SO_4 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ per gram of $\text{Ce}(\text{OH})_3\text{-Zr}(\text{OH})_4$ gel. This process was performed under mechanical stirring and maintained for 12 h. Subsequently water was removed in a rotary evaporation, and finally dried at 110 °C for 3 h and calcined at 650 °C for 4 h.

The catalysts are labelled hereafter as x- SO_4 for the catalysts prepared by sulfation of the x-ZrCeO substrates where x denotes the Zr/Ce atomic ratio and as x- S_2O_8 for the catalysts series prepared by persulfation of the x-ZrCeO substrates.

2.2. Characterization techniques

Several characterization techniques were used to analyse the texture, structure, acidity and surface of the catalysts with the aim to explain the performance in the methane partial oxidation reaction. Textural properties were evaluated by N_2 adsorption-desorption isotherms of the samples recorded at liquid nitrogen temperature with a Micromeritics ASAP 2000 apparatus. Samples were degassed at 200 °C under vacuum overnight. Specific areas were calculated by applying the BET method within the

relative pressure range $P/P_0 = 0.05\text{--}0.30$ of the isotherms. Moreover, the pore volume and pore size of the samples were calculated by Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction (XRD) patterns were recorded on a Seifert 3000 powder diffractometer operating with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$) generated at 40 kV and 40 mA. Scans were recorded at a rate of $0.02^\circ/\text{s}$ for 2θ diffraction angles between 10° and 90° .

Temperature programmed desorption (TPD) measurements were carried out on a Micromeritics TPR/TPD 2900 equipment. Before each TPD experiment, 50 mg of catalyst sample was introduced in a U-shape quartz tube and outgassed in a He flow of 40 mL/min at 150°C for 30 minutes. Ammonia was adsorbed by exposing the outgassed sample to a stream containing 5 vol% NH_3 in He for 30 minutes at 100°C and then purged with helium at this temperature for 15 min to remove physisorbed ammonia. Desorption of ammonia was carried out in He flow by increasing the temperature to 900°C at rate of $15^\circ\text{C}/\text{min}$ with a flow rate of 40 mL/min while monitoring the evolved NH_3 using a thermal conductivity detector. Peak areas were calibrated by injecting known amounts of ammonia.

X-ray photoelectron spectra (XPS) were recorded on a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and $\text{Mg K}\alpha$ ($h\nu = 1253.6\text{ eV}$) X-ray source (12 kV and 10 mA). The powder samples were degassed at 150°C for 1 h before being moved into the analysis chamber. Charge effects on the samples were corrected by fixing the binding energies of C1s peak at 284.8 eV due to adventitious carbon. This reference gave binding energies values with accuracy of $\pm 0.1\text{ eV}$. Data treatment was performed using “XPS peak” software. The spectra were decomposed with the least square fitting routine using Gaussian/Lorentzian function and after subtracting a Shirley

background. Atomic concentrations were calculated from peak areas normalized by atomic sensitivity areas [2222].

2.3 Activity tests

The catalyst performance for the direct partial oxidation of methane to oxygenates was evaluated in a fixed bed quartz reactor (4 mm ID, 23 cm length) located inside a vertical furnace. The catalyst was placed between quartz wool plugs in the middle of the reactor tube. The temperature of the catalyst bed (20 mg) was measured by a thermocouple located inside a coaxially centred quartz cover. A mixture of $N_2 : CH_4 : O_2 = 15.5 : 9 : 1$ (molar), with a total gas flow of 56.5 mL/min (2825 mL/min·g) at atmospheric pressure was used. Flow rates were adjusted by mass flow controllers, and all gases were mixed prior to reach the reactor. The effluents of the reactor and feed stream were analyzed by on line Gas Chromatograph (GC) provided with a Thermal Conductivity Detector (TCD), using a Carboxen-1006 PLOT column (SUPELCO 25461) and He as a carrier gas. The outlet of the reactor to the injection port of GC was heated up to 150 °C in order to avoid water condensation and formaldehyde polymerization.

3. Results and Discussion

3.1 Textural properties

Specific surface areas were calculated by the BET method from the nitrogen adsorption-desorption isotherms recorded at liquid nitrogen temperature. The values of BET areas of the catalysts are summarized in Table 1. The two sulfated ZrCeO samples ($x-SO_4$ and $x-S_2O_8$) show type IV isotherms (Figure 1), typical of mesoporous and macroporous solids. All the samples display, to a greater or lesser extent, a H3 hysteresis loop, in

which liquid nitrogen evaporation commences immediately upon pressure reduction. According to IUPAC, this behaviour is observed for systems containing aggregates of plate-like particles giving rise to slit-shaped pores. In the relative pressure range of 0.7–1, the loop is originated from larger and usually disordered interparticle pores [233,244].

Figure 1. N₂ adsorption-desorption isotherms of both (a) x-SO₄ and (b) x-S₂O₈ samples.

The surface areas of the catalysts are between 4 and 20 m²/g for the x-SO₄ sulfated catalyst series. For the x-S₂O₈ persulfated catalyst series, the surface areas increase with increasing the Zr/Ce molar ratio from 10 m²/g for 01-S₂O₈ up to 53 m²/g for 15-S₂O₈. As it will see below in the section of thermal decomposition of sulfate species, it is likely that BET areas decrease due to the loss of sulfur. Sulfur species are indeed known

to preserve the surface area as was previously understood in the case of the Ce-free sulfated zirconia [245].

Table 1. BET areas and acidity of x-SO₄ and x-S₂O₈ catalysts

Catalyst	BET (m ² /g)	Acidity (μmol NH ₃ /g _{cat})	
		W*, M*	S*
01-SO ₄	8.6	292.6	17.6
05-SO ₄	5.9	160.6	85.4
10-SO ₄	20.2	257.0	30.5
15-SO ₄	4.1	396.4	66.7
01-S ₂ O ₈	10.0	166.8	14.3
05-S ₂ O ₈	13.5	108.7	31.3
10-S ₂ O ₈	46.6	256.3	39.5
15-S ₂ O ₈	53.1	255.0	37.5

*W, M and S refer to weak, medium and strong acid sites, respectively.

3.2. Structural characterization

Figure 2 shows the XRD patterns of x-SO₄ (Fig. 2a) and x-S₂O₈ (Fig. 2b) samples. Both catalyst series calcined at 650 °C show rather low crystallinity for Zr/Ce ratios 1:1 and then increases with the increase the Zr/Ce ratio from 1:1 to 15:1. Major phases identified in the two catalysts series are tetragonal ZrO₂ (*t*-ZrO₂, space group P42/nmc) and monoclinic ZrO₂ (*m*-ZrO₂, space group P21/c). For the sake of simplicity, no

labelling for many other diffraction lines which include overlapping contributions of *t*-ZrO₂ and *m*-ZrO₂ was added.

The 05-SO₄ catalyst also display lines of ZrOSO₄ (Zr oxysulfate), as well as some monoclinic ZrO₂ phases. The diffraction pattern corresponding to 10-SO₄ catalyst contains diffraction lines of *t*-ZrO₂ and *m*-ZrO₂ together with a sulfated and hydrated zirconium (IV) (Zr(SO₄)₂·4H₂O) phase. In addition, sample 15-SO₄ displays not only the *t*-ZrO₂ and *m*-ZrO₂ phases but also a ZrOSO₄ one. Sulfate retards the crystallization of zirconia, decreases crystallite size and increases the amount of zirconia in tetragonal phase. This is due to the influence of impregnated surface sulfate groups, which prevent the phase modification in the surface region from undergoing transformation [266,277]. The diffraction patterns of x-S₂O₈ samples show only a mixture of *t*-ZrO₂ and *m*-ZrO₂. Samples 05-S₂O₈ and 15-S₂O₈ display *t*-ZrO₂ with oxygen vacancies. The presence of oxygen vacancies is a widely known feature of tetragonal zirconia, the predominant phase of crystalline sulfated-ZrO₂ catalysts.

Figure 2. XRD patterns of (a) $x\text{-SO}_4$ and (b) $x\text{-S}_2\text{O}_8$ catalyst series. Phases identified: $\bullet$, ZrO_2 -tetragonal, $\blacklozenge$, ZrO_2 -monoclinic, $\blacktriangle$, ZrOSO_4 , $\blacklozenge$, $\text{Zr(SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

During the calcination of the sulfated Zr-Ce hydroxide, the sulfate could act as a stabilizer of oxygen vacancies, possibly by a charge compensating mechanism. Srinivasan *et al.* [288] presented evidence showing that surface sites adsorbing oxygen at low temperatures (25–220 °C) are responsible for the tetragonal to monoclinic transformation at low temperatures. The incorporation of sulfate covers these sites and inhibits the tetragonal to monoclinic transformation. The presence of oxygen vacancies could also stabilize the tetragonal crystalline phase and lower the oxidation state of some of the surface cations, which could become Zr^{3+} sites [277,299]. As indicate the intensity of diffraction lines corresponding to monoclinic zirconia, the incorporation of

persulfate groups on Zr–CeO support has a lesser effect than the sulfates, retarding the transformation of tetragonal phase to monoclinic. Although incorporation of ceria into sulfated zirconia did not allow establishing a relationship between the proportion of tetragonal and monoclinic zirconia, it has been reported that Ce addition restrained the phase transition of ZrO₂ from tetragonal to monoclinic, if the samples were calcined at higher temperature, preventing from agglomeration [8].

The samples with lower Zr/Ce ratio exhibit broad diffraction patterns due to small particle size and poor crystallinity, being crystallinity increased with increasing Zr/Ce ratio. The sample 10–S₂O₈ was found to be the most crystalline one. Besides this, none of the samples analyzed developed a (Zr,Ce)O₂ solid solution. Nevertheless, the presence small crystallites with sizes below 2–3 nm of such a (Zr,Ce)O₂ phase cannot be fully discarded.

3.3. Thermal decomposition of sulfate species

Sulfate and persulfate species developed on the surface of x–SO₄ and x–S₂O₈ samples decompose thermally at temperatures somewhat above 550 °C [3030]. Accordingly, thermal decomposition experiments were performed with the objective to evaluate the range of temperatures where the decomposition occurs. Figure 3 show thermal desorption profiles of x–SO₄ (Fig. 3a) and x–S₂O₈ (Fig. 3b) samples. The general trend observed is that the maximum of SO_x desorption profiles shifts a little to higher temperatures when the Zr/Ce ratio decreases (Fig.3), this being more clear and evident for x–S₂O₈ samples. Thus, the maximum of desorption peak for 15–SO₄ sample appears at about 690 °C while it is shifted to 743 °C for the 01–SO₄. In the case of persulfated series (Fig. 3b), the maximum of desorption peak for 15–S₂O₈ sample appears at about 695 °C while it is shifted to 740 °C for the 01–S₂O₈.

Figure 3. SO₂ desorption profiles of (a) x-SO₄ and (b) x-S₂O₈ samples.

For x-S₂O₈ samples, the amount of SO_x released is maximum for 01-S₂O₈ and drops to a minimum for the 15-S₂O₈ sample. For x-SO₄ samples, quantitative data indicate that the amounts of SO_x released are rather high and similar for samples with x = 1, 5 and 15. The exception is the 10-SO₄ sample which shows much lower amount of released SO_x. It is emphasized that this sample has a much higher BET area (Table 1).

Then, these results obtained following desorption of SO_x moieties from the sulfate/persulfate ZrCeO samples under inert atmosphere (Figure 3) indicate that the samples do not release SO_x at least up to 600 °C; at higher temperature they start decomposing to SO_x [28]. If the quantities of desorbed SO_x from the x-S₂O₈ samples are compared, it is observed that largest amount of desorbed SO_x occurs, in each series, for

the samples 01-SO₄ and 01-S₂O₈, which in turn possess the highest Ce-loading. Moreover, the position of the maximum of desorption peak in these samples are located at the highest temperature, and the convoluted profile shifts to lower temperatures upon increasing the Zr/Ce ratio. These observations indicate that sulfate and persulfate species appear to be more stable in the Ce-rich samples which in turn show lower BET areas. This fact suggests that sulfate and persulfate species probably anchor on Ce sites during the sulfation-persulfation treatment, increasing acid strength. Thus, the thermostability of these sulfate species is found to be strongly dependent on the composition/structure of the parent (Ce,Zr)O₂ systems.

3.4. Acidity

Acidity of both sulfated and persulfated samples has been determined by ammonia TPD. NH₃ desorption profiles are shown in Figure 4.

Figure 4. NH_3 -TPD profiles of (a) x-SO_4 and (b) $\text{x-S}_2\text{O}_8$ samples

The NH_3 -TPD profiles of x-SO_4 and $\text{x-S}_2\text{O}_8$ series show a main contribution in the 100–400 °C temperature range, related to weak (W) and moderate (M) acid sites, and a small desorption peak between 400–600°C, related to strong acid sites (S). In x-SO_4 series the relative maxima of the main desorption peak are shifted to higher temperatures depending on the Zr/Ce ratio, being found the following order from low to high temperature: $15\text{-SO}_4 < 05\text{-SO}_4 < 01\text{-SO}_4 < 10\text{-SO}_4$. This order is the same than that followed by the BET areas values (Table 1), which suggest that the strength of the acid sites is linked to the surface area. Concerning the persulfated series, it is not found a trend between the strength of weak and moderate acid sites and the Zr/Ce ratio. It is observed that the maximum is slightly shifted to higher temperatures for the sample $01\text{-S}_2\text{O}_8$. The amounts of ammonia desorbed for all the samples are collected in Table 1. The smaller area of desorption peaks observed for persulfated samples in comparison to sulfated counterparts can be considered as an indication for the presence of a lesser surface proportion of acid sites, with the exception of sample $10\text{-S}_2\text{O}_8$, whose acidity amount is some higher than that found for 10-SO_4 .

Considering these results and, as previously commented, the prepared samples mainly contain acid sites of weak and moderate acid strength. With the exception of sulfated and persulfated samples with ratio $\text{Zr/Ce}=1$, for both series, the increase in acidity (amount of acid sites) is proportional to the increase of Zr/Ce ratio, being found a plateau for persulfated samples, when Zr/Ce achieves a value of 10. The comparison of Figures 3 and 4 reveal that sulfated samples are more acid than persulfated counterparts.

1 It is found that both sulfate and persulfate groups generate surface acidity, when
2 adsorbed on mixed oxide supports. Desorption at temperatures higher than 550 °C,
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4 indicate that sulfate and persulfate groups generate strong acidity, in these mixed
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6 oxides, containing both strong Brønsted and Lewis acid sites [3131]. Sulfate and
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8 persulfate species, by attracting electrons, can generate Lewis acid sites on the oxide
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10 surfaces. These Lewis acid sites increase the Brønsted acid strength of the surface
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12 hydroxyl groups.
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17 3.5. Surface Analysis

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21 Photoelectron spectroscopy (XPS) was used to identify the chemical state of the
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23 elements and also to quantify surface population. The high resolution Zr3d, Ce3d, O1s
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25 and S2p spectra were recorded for the two x-SO₄ and x-S₂O₈ catalyst series and they are
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27 collected in Figure 5 for the representative 10-SO₄ sample. The binding energy of the
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29 most intense Zr3d_{5/2} peak appears at almost constant value irrespective of the type of
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31 sulfate species incorporated (182.1–182.2 eV) which is typical of Zr⁴⁺ ions in an
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33 environment of O²⁻ ions [3232]. The S2p peak shows essentially constant binding
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35 energy (168.6–168.7 eV) which is characteristic of sulfates. The O1s peak was fitted in
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37 all catalysts into two components: one place at ca. 530 eV which is characteristic of O–
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39 Zr/O–Ce bonds and a second one located at about 2 eV higher binding energy which
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41 may involve contributions from SO₄²⁻ and OH groups. The Ce3d spectrum is rather
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43 complex and has been evaluated as described in the literature [29,30]. Table 2 compiles
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45 the components in the Ce3d spectrum and their binding energies. Both Ce⁴⁺ and Ce³⁺
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47 species, with the latter being dominant, are present on the surface of the x-SO₄ and x–
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49 S₂O₈ samples and their relative percentages were calculated as described in the literature
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51 [333,344]. The surface concentration of sulfated species was determined by the
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S/(Zr+Ce) atomic ratio. For persulfated samples, the general trend observed is that this ratio decreases with increasing Zr/Ce ratio.

Table 2. Surface atomic ratios and cerium atomic percentages of both catalyst series

Sample	Atomic ratios			
	Zr/Ce	S/(Zr+Ce)	Ce ⁴⁺	Ce ³⁺
01-SO ₄	4.93	0.371	18	82
05-SO ₄	7.87	0.430	20	80
10-SO ₄	17.86	0.186	23	77
15-SO ₄	16.13	0.446	26	74
01-S ₂ O ₈	3.57	0.410	21	79
05-S ₂ O ₈	8.20	0.265	23	77
10-S ₂ O ₈	15.64	0.214	19	81
15-S ₂ O ₈	16.70	0.164	25	75

Figure 5. High resolution Zr3d, O1s, Ce3d and S2p core level spectra of the representative 10-SO₄ sample.

Green area in Ce3d energy region belongs to inner Zr level.

Agreement between the quantities of SO_x released from the persulfated/sulfated samples and the surface exposure of sulfate species, as measured by the $\text{S}/(\text{Ce}+\text{Zr})$ atomic ratio derived from quantitative XPS measurements, was obtained. Thus, Figure 6 shows a close relationship between the amounts of SO_x released (both per g of catalyst and per

square meter of catalyst) and surface density of persulfate/sulfate species evaluated by the $\text{S}/(\text{Ce}+\text{Zr})$ ratio for both x-SO_4 and $\text{x-S}_2\text{O}_8$ samples.

Figure 6. Relationship between the amount of SO_x released (per gram and per square meter of catalyst) upon thermal desorption and the relative S concentration evaluated by XPS for the two catalyst series. (●) persulfated samples ($\text{x-S}_2\text{O}_8$); (◆) sulfated samples (x-SO_4).

Emphasis is also paid in the heterogeneities observed in surface composition. This is derived from the comparison of the experimental Zr/Ce atomic ratios derived from XPS (Table 2, 2nd column) with the nominal Zr/Ce ones. It is evident that surface became Zr-enriched specifically in the region of lower Zr/Ce ratios. Moreover, an important fraction of ceria is reduced to Ce^{3+} oxide. This means that the $\text{Ce}(\text{OH})_3$ phase

precipitated during preparation did not fully oxidized to Ce^{4+} oxide during air-calcination in both catalyst series. The Ce^{4+} percentages were in the range 18–26% in x-SO₄ samples and in the range 21–25% in the x-S₂O₈ samples, increasing only slightly with the increase of Zr/Ce ratio.

3.6. Catalyst performance

All sulfated and persulfated samples were tested for the selective oxidation of methane under fixed reaction conditions. The results recorded after 4 h on-stream, are compiled in Figure 7 (x-SO₄ series) and Figure 8 (x-S₂O₈ series). Activity and selectivity toward different products depend on the Zr/Ce ratio in the catalyst, the space velocity, the reaction temperature and the CH₄/O₂ molar ratio in the feed. Since the catalytic tests were performed by keeping constant reaction temperature, space velocity and CH₄/O₂ ratio, differences in CH₄ conversion and selectivity patterns of the x-SO₄ (Fig. 7) and x-S₂O₈ (Fig. 8) catalyst series can be associated to the catalyst properties. Methane conversions and yields to CO, CO₂ and C₁ oxygenates (formaldehyde or methanol) are compiled in Table 3.

Figure 7. CH₄ conversion, selectivity to CO and CO₂, and HCHO yield of the catalyst of the x-SO₄ series.

Reaction conditions: T = 650 °C, CH₄/O₂ = 9:1, space velocity, 2825 mLN/min·g

The CH₄ conversion are around 6.0–6.5% for all the catalysts, except for the 05-S₂O₈, which produces a conversion some higher than 2% (table 3), which are not so far from the theoretical value (9.0 %) expected taking into account the high fuel-rich conditions (CH₄/O₂ = 9) used in this work. A comparison of the performance of different catalysts with that obtained in homogeneous regime, in which no conversion of methane is found, evidence the net contribution of these acidic catalysts to the activation of methane and, more, considering the high space velocity used in catalytic tests. Methane conversion values achieved indicate that the acid sites of the catalyst surface are involved in the

1 activation of CH₄ molecules [355], although also producing high selectivity toward
2 deep oxidation reactions of C₁-oxygenates into CO_x final products.
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5 The highest selectivity to formaldehyde is obtained with a Zr-Ce ratio of 5 for both
6 sulfated and persulfated catalysts, exact values being 55 and 161 g/h·kg catalyst,
7 respectively. This behavior seems to be related to the surface acidity. Thus, above
8 catalysts are those with a lower surface density of acid sites (246 and 140 μmol
9 NH₃/g_{cat}, respectively, Table 1). It is worth mentioning that 05-S₂O₈ catalyst is
10 relatively high selective to formaldehyde formation. Formaldehyde formation is limited
11 by the low methane conversion found with this catalyst. This fact is explained by its
12 very low acidity, which has an important role activating methane molecule. If surface
13 acidity and CO₂ selectivity are compared, some direct relationship is found, pointing out
14 that certain acidity is favorable to activate methane and produce C₁ oxygenates, but if
15 acidity is above a certain value, it promotes the further oxidation of these valuable
16 compounds to carbon dioxide. For sulfated catalysts, those with a higher surface density
17 of acid sites are those more selective to combustion (with the highest CO₂ selectivity,
18 around 79%).
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Figure 8. Catalytic results as CH₄ conversion, selectivity to CO and CO₂, and HCHO yield of the catalysts of the x-S₂O₈ series. Reaction conditions: T = 650 °C, CH₄/O₂ = 9:1, space velocity, 2825 mL/min·g

It should be highlighted that the catalyst that produce the highest yield to C₁ oxygenates (methanol) is 10-S₂O₈, which is characterized by a relatively high surface area and a medium acidity.

Table 3. Catalytic results as CH₄ conversion and CO, CO₂, and C₁ oxygenates yields reached with the catalyst of the x-SO₄ and x-S₂O₈ series. Reaction conditions: T = 650 °C, CH₄/O₂ = 9:1, space velocity, 2825 mL/min·g

Sample	CH ₄ conv. (%)	Yield (%)

		CO	CO ₂	C1 oxygenates
01-SO ₄	6.3	1.3	5.0	0
05-SO ₄	6.4	2.8	3.5	0.1 (55 g HCHO/h·kg cat.)
10-SO ₄	6.1	2.4	3.7	0
15-SO ₄	6.3	1.3	5.0	0
01-S ₂ O ₈	5.8	1.7	4.0	0.1(54 g HCHO/h·kg cat.)
05-S ₂ O ₈	2.3	1.5	0.7	0.1 (161 g HCHO/h·kg cat.)
10-S ₂ O ₈	6.5	0.9	5.4	0.2 (221 g CH ₃ OH/h·kg cat.)
15-S ₂ O ₈	6.4	0.8	5.6	0
*in brackets, HCHO yield expressed as g HCHO/h·kg catalyst				

The formation of SO_x during calcination promotes the electron-accepting ability for the metal atoms (Lewis acidity), making the complex acidic. Both acidity and redox properties of all catalyst series make them appropriate to activate the C-H bond of CH₄ molecule. Activity performance of the two catalyst series indicated that activity is strongly dependent on these properties. Working under fuel-rich conditions (CH₄/O₂ = 9) and high reaction temperatures (650 °C), the CH₄ conversion on most of the catalysts was not far to the theoretical value expected from a 100% O₂ conversion. The comparison of catalyst performances indicate that catalyst acid sites participate in the activation of CH₄ molecules, increasing when acidity is a certain range. It should be noted that the catalysts with a similar S/Ce+Zr ratio (Table 2), 05-SO₄ and 01-S₂O₈ produce similar yields to formaldehyde (table 3). The importance of both acid sites surface density and sulfur species is evidenced when we compare between 10-S₂O₈ and

15-S₂O₈, both with similar amount of acid sites. The high yield to methanol showed by 10-S₂O₈ catalyst seems to be also related with a relatively high proportion of SO_x species. Notwithstanding, it should be emphasized that the product of interest (HCHO) is much more reactive than the starting CH₄ molecules, which makes its selectivity to be low. The strong activity-selectivity dependence observed in the target reaction points out to the use of milder reaction conditions, i.e., lower reaction temperatures and fuel-rich conditions, as to minimize the extent of deep oxidation reactions, by controlling the surface acidity.

4. Conclusions

From the results obtained in this work, the following conclusions can be obtained: (i) The characterization of sulfated and persulfated zirconia-ceria samples revealed differences in textural, structural and acid properties depending on the Zr/Ce ratio and on the sulfate anion type; (ii) In both series, acid site density was found to increase with the Zr/Ce ratio; however, acid strength decreased with Zr/Ce ratio (iii) The two x-SO₄ and x-S₂O₈ catalyst series were found active for methane activation, but poorly selective for C₁ oxygenates formation; finally, (iv) The most selective catalysts for C₁ oxygenates formation and less selective toward combustion are those with Zr/Ce = 5, which have medium acidity.

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Table 1:

Table 1. BET areas and acidity of x-SO ₄ and x-S ₂ O ₈ catalysts			
Catalyst	BET (m ² /g)	Acidity (μmol NH ₃ /g _{cat})	
		W*, M*	S*
01-SO ₄	8.6	292.6	17.6
05-SO ₄	5.9	160.6	85.4
10-SO ₄	20.2	257.0	30.5
15-SO ₄	4.1	396.4	66.7
01-S ₂ O ₈	10.0	166.8	14.3
05-S ₂ O ₈	13.5	108.7	31.3
10-S ₂ O ₈	46.6	256.3	39.5
15-S ₂ O ₈	53.1	255.0	37.5

*W, M and S refer to weak, medium and strong acid sites, respectively.

Table 2:

Table 2. Surface atomic ratios and cerium atomic percentages of both catalyst series

Sample	Atomic ratios			
	Zr/Ce	S/(Zr+Ce)	Ce ⁴⁺	Ce ³⁺
01-SO ₄	4.93	0.371	18	82
05-SO ₄	7.87	0.430	20	80
10-SO ₄	17.86	0.186	23	77
15-SO ₄	16.13	0.446	26	74
01-S ₂ O ₈	3.57	0.410	21	79
05-S ₂ O ₈	8.20	0.265	23	77
10-S ₂ O ₈	15.64	0.214	19	81
15-S ₂ O ₈	16.70	0.164	25	75

Table 3:

Table 3. Catalytic results as CH₄ conversion and CO, CO₂, and C₁ oxygenates yields reached with the catalyst of the x-SO₄ and x-S₂O₈ series. Reaction conditions: T = 650 °C, CH₄/O₂ = 9:1, space velocity, 2825 mL/min·g

Sample	CH ₄ conv. (%)	Yield (%)		
		CO	CO ₂	C1 oxygenates
01-SO ₄	6.3	1.3	5.0	0
05-SO ₄	6.4	2.8	3.5	0.1 (55 g HCHO/h·kg cat.)
10-SO ₄	6.1	2.4	3.7	0
15-SO ₄	6.3	1.3	5.0	0
01-S ₂ O ₈	5.8	1.7	4.0	0.1 (54 g HCHO/h·kg cat.)
05-S ₂ O ₈	2.3	1.5	0.7	0.1 (161 g HCHO/h·kg cat.)
10-S ₂ O ₈	6.5	0.9	5.4	0.2 (221 g CH ₃ OH/h·kg cat.)
15-S ₂ O ₈	6.4	0.8	5.6	0

*in brackets, HCHO yield expressed as g HCHO/h·kg catalyst

Figure 1:

Figure 1. N₂ adsorption-desorption isotherms of both (a) x-SO₄ and (b) x-S₂O₈ samples.

Figure 2:

Figure 2. XRD patterns of (a) $x\text{-SO}_4$ and (b) $x\text{-S}_2\text{O}_8$ catalyst series. Phases identified: ●, ZrO_2 -tetragonal, ◆, ZrO_2 -monoclinic, ▲, ZrOSO_4 , ✕, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Figure 3:

Figure 3. SO₂ desorption profiles of (a) x-SO₄ and (b) x-S₂O₈ samples.

Figure 4:

Figure 4. NH₃-TPD profiles of (a) $x\text{-SO}_4$ and (b) $x\text{-S}_2\text{O}_8$ samples

Figure 5:

Figure 5. High resolution Zr3d, O1s, Ce3d and S2p core level spectra of the representative 10-SO₄ sample. Green area in Ce3d energy region belongs to inner Zr level.

Figure 6:

Figure 6. Relationship between the amount of SO_x released (per gram and per square meter of catalyst) upon thermal desorption and the relative S concentration evaluated by XPS for the two catalyst series. (●) persulfated samples (x-S₂O₈); (◆) sulfated samples (x-SO₄).

Figure 7:

Figure 7. CH₄ conversion, selectivity to CO and CO₂, and HCHO yield of the catalyst of the x-SO₄ series. Reaction conditions: T = 650 °C, CH₄/O₂ = 9:1, space velocity, 2825 mLN/min·g

Figure 8:

Figure 8. Catalytic results as CH₄ conversion, selectivity to CO and CO₂, and HCHO yield of the catalysts of the x-S₂O₈ series. Reaction conditions: T = 650 °C, CH₄/O₂ = 9:1, space velocity, 2825 mL/min·g